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Anodic dissolution and disintegration of tin and valency of the tin ions going into solution

Mrityunjoy Dutta

ANODIC DISSOLUTION AND DISINTEGRATION OF TIN AND VALENCY OF THE TIN IONS GOING INTO SOLUTION

BY

MRITYUNJOY DUTTA

A

THESIS

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M. E. Straumanis (Advisor) William J. James

D. E. Day Fred Kissling

ABSTRACT

Tin was found to form solely Sn^{2+} ions when dissolving anodically from a tin-amalgam in aqueous acid solutions of HCl, H_2SO_4, $HClO_4$, H_3PO_4, HNO_3, and HF, without the use of an external current.

Blackening of the anodic surface was observed during dissolution in HCl and $HClO_4$, but no dropping down of particles. The black particles were of metallic tin and were in contact with the metal surface, protruding from it. These protruding particles are formed during anodic dissolution due to preferential attack at the grain boundaries, deformation twins, and other imperfections causing mountains of tin on the anode surface.

There was no deviation from Faraday's law within the error limits of the measurements.

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I. INTRODUCTION

Tin is one of the least plentiful and highest priced of the common non-ferrous metals. The chief applications for tin are coating of steel (tin plate), solder, bronze and babbitt. Tin coatings are applied to ferrous materials and copper alloys in order to increase their resistance to corrosion. Tin retains its brightness well during atmospheric exposure. In aqueous media, tin reacts with both strong acids and strong bases, but is relatively resistant to nearly neutral solutions. Corrosion is greatly accelerated by the presence of oxygen. Normally, tin is coated with a thin invisible film of stannic oxide, which may be removed by acids or alkalies, or may be penetrated locally so that pits develop. Corrosion by pitting is more common in nearly neutral solutions than corrosion by general attack. When tin is used as a protective coating, corrosion is usually localized at pinholes through the coating.

The increasing demand for protective coatings on metals and for non-corrosive alloys has stimulated extensive research on the fundamental behavior of metals in corrosive media.

One of the problems still unsolved is the nature of the mechanism of the anodic dissolution of metals like beryllium, zinc, magnesium, cadmium, tin, aluminum, iron in aqueous salt solutions. It has been reported in the literature that these metals show discrepancies which often arise between coulometric data and the weight loss of metal electrodes in various media. Several investigators have proposed different and opposing theories to explain the above deviation.

The purpose of the present investigation was to obtain experimental data for the anodic dissolution of tin in various electrolytes using liquid tin-amalgam and solid tin as an anode, and also to study the phenomena of disintegration for this particular metal.

II. LITERATURE REVIEW

The fact that certain metals do not appear to obey Faraday's law during anodic dissolution in certain electrolytes has been known for a long time. In recent years more than 100 per cent current efficiency has been observed for the anodic dissolution of magnesium, zinc, iron, aluminum, beryllium, indium, gallium, cadmium, tin and titanium.

In 1911, White (1) studied the anodic dissolution of tin in various electrolytes. Assuming the normal valency of tin as 2, he observed abnormally high current efficiencies for the anodic dissolution of tin in aqueous solutions of sodium nitrate ($NaNO_3$), and ammonium nitrate (NH_4NO_3); and abnormally low current efficiencies in sodium nitrite ($NaNO_2$) and sodium tartrate ($Na_2C_4H_4O_6$). For the explanation of the observed high current efficiency, he suggested the possibility of monovalent tin ion formation.

The "uncommon valence theory" in which anodic valencies lower than normally observed in electrolytic processes has been since then advocated by many authors. Davidson, Kleinberg, and co-workers (2, 3, 4, 5, 6) favor the uncommon valence theory as the mechanism. Even the negative difference effect observed by Thiel and Eckell (7) was explained by this mechanism.

Rumpel, Davidson, and Kleinberg (8) studied the anodic dissolution of tin in NaCl, $NaC_2H_3O_2$, $SnCl_2$, $KClO_3$, $NaNO_3$, $Sn(NO_3)_2$, $NaC_2H_3O_2$-$NaNO_3$ mixture, and KCl-$NaNO_3$ mixture. They employed an electrolytic cell into which a sintered glass membrane was inserted between electrode compartments to facilitate analysis of the contents of the anode compartment without interference by cathodic products. A flow of inert gas (nitrogen or helium) above the electrolyte prevented oxidation by air of products formed during electrolysis. Tin in the form of sticks was used for electrodes. Direct current at voltages up to 250 volts was obtained from a rectified and filtered a.c. source.

Experiments conducted with NaCl, $NaC_2H_3O_2$, and $SnCl_2$ established the valency of Sn-ions going into solution as 2. However, in $KClO_3$, a valency of 1.81, in KCl-$NaNO_3$ mixture - 1.80, in $NaC_2H_3O_2$-$NaNO_3$ mixture - 1.17, and in aqueous solutions of $NaNO_3$ valencies ranging from 1.02 to 1.33 were obtained. In two further tests in $NaNO_3$ solution, a liquid tin-amalgam was used as an anode, whereas the cathode was of the same metal as before. Electroplating of the anolyte was used for quantitative determination of anodic dissolution. The results of these tests showed that the valency of Sn-ions going into solution was as low as 1.27 and 1.40 at

current densities 2.5 and 10.0 milliamperes per centimeter square, respectively.

On the basis of these results the mentioned authors postulated that the first step in the anodic oxidation of tin is the production of univalent tin ions. It was assumed that in systems in which tin shows a valency of 2, all the univalent intermediate ions return to the anode and are there oxidized electrolytically to the +2 state (Eq. 2).

The lower valency obtained in the case of $NaNO_3$ or $KClO_3$ electrolytes is explained by the assumption that part of the univalent Sn-ions is oxidized chemically (non-electrolytically) whereas the other part returns to the anode and is oxidized electrolytically to the +2 state. The equations expressing the mechanism in $NaNO_3$ are as follows:

$$Sn = Sn^{+} + e^{-} \quad \text{(electrolytic)} \qquad (1)$$

$$Sn^{+} = Sn^{2+} + e^{-} \quad \text{(electrolytic)} \qquad (2)$$

$$2\,Sn^{+} + NO_3^{-} + 2\,H^{+} = 2\,Sn^{2+} + NO_2^{-} + H_2O \qquad (3)$$

$$8\,Sn^{+} + NO_3^{-} + 10\,H^{+} = 8\,Sn^{2+} + NH_4^{+} + 3H_2O \qquad (4)$$

$$Sn^{2+} + (x+1)\,H_2O \rightleftharpoons SnO.x\,H_2O + 2\,H^{+} \qquad (5)$$

$$2\,Sn^{2+} + NO_2^{-} + (2y+3)\,H_2O = 2\,SnO_2.y\,H_2O + NH_2OH + 3\,H^{+} \qquad (6)$$

To explain the observed valency of 1.17 in $NaNO_3$ electrolyte they assumed 71 per cent of the total quantity of electricity produces Sn^{+} ions which are chemically oxidized in reactions (3) and (4), while the other 29 per cent produces Sn^{2+} cations by consecutive reactions (1) and (2).

As early as 1916, E. Newbery (9) observed the formation of a black coating on the anodic surface during the study of anodic overvoltage of tin in sulfuric acid. The same observation was made during electrolysis in HCl by Vaubel (10) who noted a black powder on the anode which dissolved only very slowly even in the concentrated acid. It was thought that the deposit was a peculiar modification of the metal which was produced by the reduction of stannous chloride by nascent hydrogen.

Jeffery (11) observed a complex tin salt formation during the electrolysis of a potassium oxalate solution with a tin anode. The anion formed was derived from Sn^{2+}. The same author found also that the anode was covered itself with a fine black adherent deposit at low current density, but spalling occurred at higher current densities.

Electrolysis of sodium stannate solution (12,13) with a tin anode produced only stannous ions at low current densities. At high current density the anode became passive

and a yellow oxide coating was formed. Under such conditions, electrolysis could be continued until all of the Sn entered the solution in a quadrivalent state.

E. Vallesi (14), using a.c. (50 cycles) and tin electrodes in a NaOH solution, reported that Sn goes into solution as Sn^{4+} and a black powdery tin deposit is formed on the anode. Later, Nakai and Kato (15) repeated the same experiments, measuring in addition the anodic potentials. The experimental polarization curves showed three stages: an anodic film in the first stage consisting of $Sn(OH)_2$ was formed and the tin went into solution as stannite (SnO_2^{2-}) ions; in the second stage, both stannite and stannate (SnO_3^{2-}) ions partially were produced and the anodic film was considered to consist of $Sn(OH)_2$ and $Sn(OH)_4$; in the third stage, oxygen was evolved at the anode which became passive, and so the current efficiency decreased considerably, even below 10 per cent.

Thus, in the recent literature, a deviation from Faraday's law during anodic dissolution was described, and characteristic appearances of the anode in various electrolytes-in the older. The latter fact agrees partially with a proposal of the "chunk effect" made by Marsch and Schaschl (16). These authors observed that when steel dissolves anodically

at a high rate, the corrosion proceeds with the removal of chunks of iron containing several atoms. Similarly for beryllium (17), it was established that simultaneously with dissolution (using no current), disintegration of beryllium into small particles occurs.

The present investigation was therefore aimed to study both of these possible phenomena of uncommon valence and disintegration in various acid aqueous solutions (HCl, HF, H_2SO_4, $HClO_4$, H_3PO_4, and HNO_3).

III. EXPERIMENTAL

The experimental plan consisted of the following major phases:

1. valency determination of tin using a liquid Sn - amalgam as anode;

2. dissolution studies with a solid tin anode;

3. examination of the black film particles by an optical microscope and by x-ray diffraction;

4. quantitative measurements of the black film formed in HCl electrolyte.

A. Valency Determination of Tin Using Liquid Sn-Amalgam as Anode.

1. Materials. The tin metal used in this investigation was of a Baker's analyzed high purity (99.99%) product. The chemical analysis of this tin is as follows:

Sn	99.996%
Pb	0.003%
Fe	0.001%

The mercury was triply distilled in this laboratory and checked for impurities by making blank experiments in the respective electrolytes.

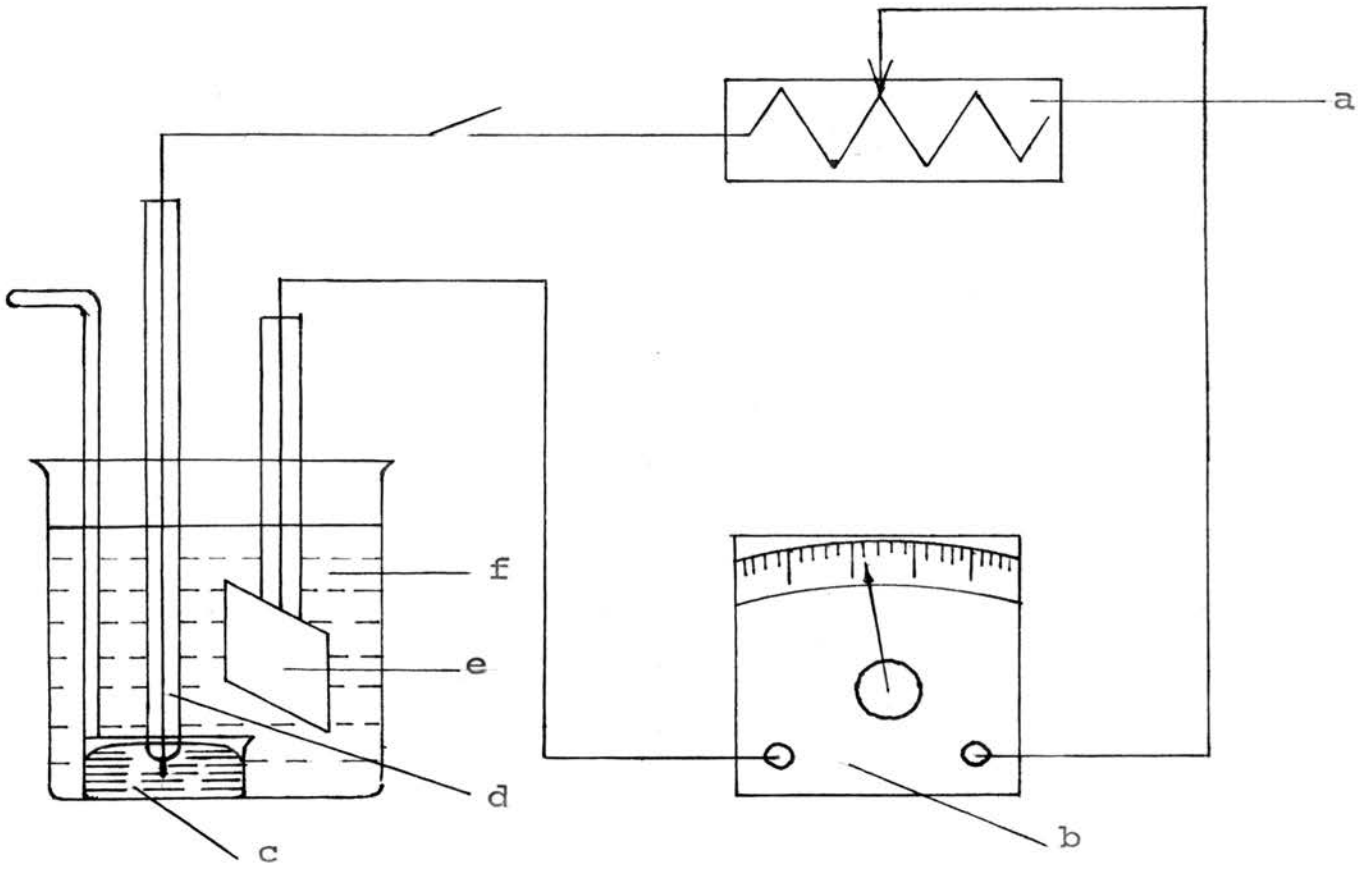
The acids used were of reagent grade obtained from the Fisher Scientific Company. The following acids were used: HCl (6, 3, 1, and 0.5 N); H_2SO_4 (18, 15, 6, 3, and 2 N); $HClO_4$ (8, 4, 3, and 1.5 N); H_3PO_4 (25, 17, and 8.5 N); HNO_3 (1 and 0.5 N); HF (6 and 3 N).

Coulometric measurements were made using a sensitive Weston direct current milliammeter of high quality.

A platinized platinum electrode was used as a cathode.

2. Apparatus. The experimental setup is shown in Figure 1. The apparatus consisted of a small beaker containing the particular electrolyte into which a small glass container holding 2 or 3 milliliters of distilled mercury was submerged. A platinum wire extending from a sealed glass tube was dipped into the mercury. The platinum wire was electrically connected to one terminal of the milliammeter through a resistance box and a switch. The other terminal of the milliammeter was connected with the platinum cathode.

3. Procedure. A piece of tin between 20 to 40 milligrams was accurately weighed on an analytical balance and dropped into the mercury. Tin dissolves in mercury forming tin-amalgam. As the circuit was closed Sn went into the solution as Sn^{2+} ions from the Sn-amalgam anode, and the



a. Variable resistance box
b. Weston direct current milliammeter
c. Shallow dish containing mercury
d. Platinum wire in a sealed glass tube
e. Platinized platinum cathode
f. Aqueous acid solution (Electrolyte).

Figure 1. Experimental setup for valence measurements by the amalgam electrode method.

free electrons flowed from the anode through the outer circuit to the platinum cathode where they discharged the hydrogen ions and thus, hydrogen gas developed at the cathode. The reactions at the anode and at the cathode are as follows, assuming only Sn^{2+} ions were formed:

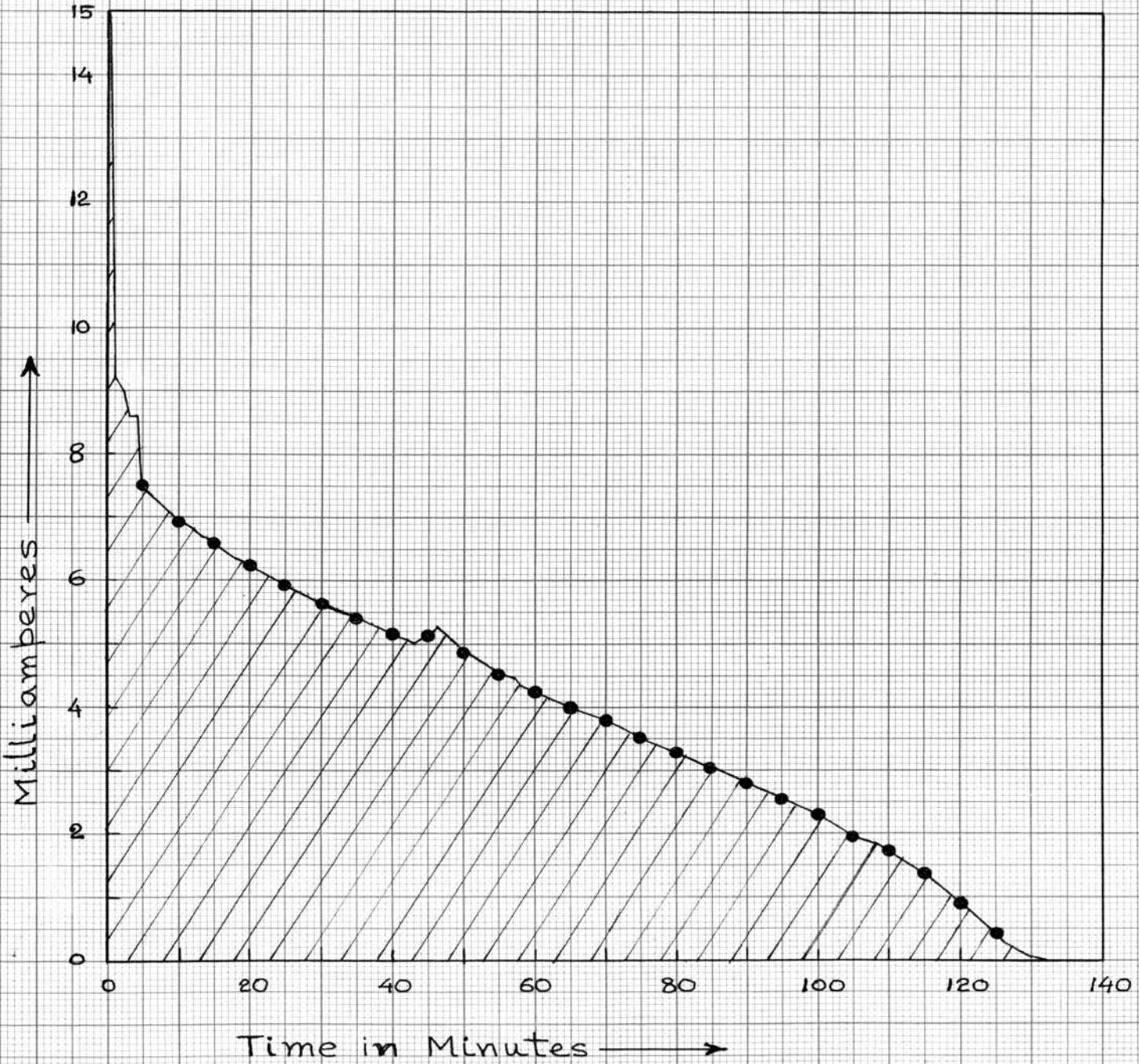
at the anode: $Sn \longrightarrow Sn^{2+} + 2\ e^-$

at the cathode: $2\ H^+ + 2\ e^- \longrightarrow H_2$

The same type of reaction occurred at the anode and cathode regardless of the acids used as electrolytes.

Tin was thus allowed to dissolve anodically from Sn-amalgam. The current was noted immediately after the circuit was closed and read at one-minute intervals until the current reached zero. These readings were plotted against time and diagrams as shown in Figure 2 were obtained. The areas under the curves were measured with a compensating planimeter. Four measurements were taken for each area by the planimeter and were averaged.

The determinations with higher concentrations of H_2SO_4 required that the amalgam be constantly stirred to break the film of difficultly soluble mercury sulfate which insulated the amalgam from the electrolyte if left alone. The same happened with H_3PO_4 as an electrolyte. To break the film a



Weight of Sn (input): 0.0195 g Acid: 1.5 N $HClO_4$
Area of Plot: 31.92 amp-sec ≡ 0.01963 g Sn compared with 0.0195 g Sn (input).

Figure 2. A typical plot of current vs. time for dissolution of tin from an amalgam electrode.

glass stirrer driven by an electric motor was used. The end of the stirrer was just touching the amalgam surface.

An added precaution with HF as an electrolyte was the protection of the exposed glass with a wax coating.

No gas bubbles were formed on the amalgam surface during anodic dissolution and thus, no local circuits were present on it.

From these tests the actual valencies of Sn-ions were calculated. The weight of the tin dissolved was compared with the weight calculated from the amount of amp-secs, assuming a valency of +2 for the Sn-ions.

4. Sample calculations. The weight of tin dissolved anodically was calculated from Faraday's law, assuming the normal oxidation state of +2, from the equation:

$$\text{Weight of Sn dissolved} = \frac{I.t.A}{F.n}$$

where I is the current in ampere,

t - the time in seconds,

A - the atomic weight of Sn (=118.69),

F - Faraday's constant (=96,487 amp-sec), and

n - the normal cationic charge of Sn (=+2).

In one test (I.t) was 40.26 amp-secs; therefore, the weight of Sn which went into solution was:

$$\frac{(40.26)(118.69)}{(96,487)\ (2)} = 0.02476 \text{ g.}$$

But the actual amount of Sn dissolved in mercury was 0.02480 g. Hence, the difference in percentage was:

$$\frac{(0.02476 - 0.02480)(100)}{(0.02480)} = -0.16\ \%$$

The valency, V, was calculated simply from the equation:

$$V = \frac{I.t.A.}{F.w}$$

where w is the weight of Sn dissolved in Hg.

The previous example gives a valency as follows:

$$V = \frac{(40.26)(118.69)}{(96,487)\ (0.02480)} = 1.996$$

5. Results. The results obtained in HCl, H_2SO_4, $HClO_4$, H_3PO_4, HNO_3, and HF are summarized in Tables I to VI.

TABLE I

Valency of Sn-ions going into Solution from Sn-Amalgam in HCl

HCl	Input of Sn	Current	Calculated amount of tin assuming Sn^{2+}	Difference	Valency	Average
N	g	amp-sec	g	%		
6.0	0.0265	43.68	0.02686	+ 1.35	2.027	
	0.0280	45.99	0.02828	+ 1.0	2.021	
	0.0222	36.66	0.02254	+ 1.53	2.031	
	0.0248	40.26	0.02476	- 0.16	1.996	
	0.0331	54.16	0.03331	+ 0.64	2.012	
	0.0409	66.215	0.04072	- 0.55	1.991	
						2.012
3.0	0.0232	37.818	0.02326	+ 0.25	2.005	
	0.0315	51.75	0.03182	+ 1.01	2.020	
	0.0280	45.086	0.02773	- 0.97	1.980	
						2.001
1.0	0.0165	26.745	0.01645	- 0.31	1.994	
	0.0171	27.76	0.01707	- 0.18	1.997	
	0.0088	14.52	0.00893	+ 1.47	2.029	
	0.0252	40.845	0.02512	- 0.3	1.993	
						2.003
0.5	0.0128	20.72	0.01274	- 0.71	1.991	1.991
					Average:	2.001

TABLE II

Valency of Sn-ions Going into Solution from Sn-Amalgam in H_2SO_4

H_2SO_4	Input of Sn	Current	Calculated amount of tin assuming Sn^{2+}	Difference	Valency	Average
N	g	amp-sec	g	%		
18.0	0.0370	60.0	0.03690	- 0.27	1.995	
	0.0387	62.688	0.03855	- 0.38	1.992	
	0.0681	111.24	0.06841	+ 0.45	2.009	
						1.998
15.0	0.0324	52.95	0.03256	+ 0.49	2.010	
	0.0486	79.44	0.04885	+ 0.51	2.010	
	0.0428	70.26	0.04321	+ 0.95	2.019	
	0.0318	51.72	0.03180	0.	2.0	
						2.009
6.0	0.0075	12.27	0.00754	+ 0.53	2.012	
	0.0057	9.37	0.00575	+ 0.87	2.022	
	0.0326	53.22	0.03273	+ 0.4	2.008	
						2.014
3.0	0.0290	47.22	0.02904	+ 0.14	2.003	
	0.0208	33.93	0.02086	+ 0.29	2.006	
	0.0175	28.59	0.01758	+ 0.45	2.009	
	0.0192	31.38	0.01929	+ 0.46	2.010	
						2.007
2.0	0.0250	40.74	0.02505	+ 0.2	2.004	2.004
					Average:	2.006

TABLE III

Valency of Sn-ions Going into Solution from Sn-Amalgam in $HClO_4$

$HClO_4$	Input of Sn	Current	Calculated amount of tin assuming Sn^{2+}	Difference	Valency	Average
N	g	amp-sec	g	%		
8.0	0.0070	11.268	0.00693	- 1.0	1.980	
	0.0227	37.26	0.02291	+ 0.92	2.019	
	0.0124	20.28	0.01247	+ 0.58	2.011	
	0.0184	29.76	0.01830	- 0.55	1.989	
	0.0349	56.70	0.03487	- 0.09	1.998	
						1.999
4.0	0.0331	54.06	0.03324	+ 0.42	2.009	2.009
3.0	0.0082	13.425	0.00825	+ 0.60	2.013	
	0.0233	37.77	0.02323	- 0.3	1.994	
	0.0101	16.62	0.01022	+ 1.18	2.024	
	0.0114	18.54	0.0114	0	2.0	
	0.0190	30.96	0.01904	+ 0.21	2.004	
						2.007
1.5	0.0085	13.83	0.0085	0	2.0	
	0.0166	26.91	0.01655	- 0.3	1.994	
	0.0195	31.92	0.01963	+ 0.66	2.013	
	0.0120	19.38	0.01192	- 0.68	1.986	
						1.998
					Average :	2.003

TABLE IV

Valency of Sn-ions going into Solution from Sn-Amalgam in H_3PO_4

H_3PO_4	Input of Sn	Current	Calculated amount of tin assuming Sn^{2+}	Difference	Valency	Average
N	g	amp-sec	g	%		
25.0	0.0119	19.416	0.01194	+ 0.33	2.006	
	0.0211	34.224	0.02105	- 0.24	1.995	
	0.0197	32.304	0.01986	+ 0.55	2.017	
	0.0286	46.512	0.0286	0	2.0	
						2.004
17.0	0.0167	27.06	0.01664	- 0.36	1.993	
	0.0174	28.392	0.01746	+ 0.34	2.007	
	0.0280	45.66	0.02808	+ 0.28	2.006	
	0.0148	24.12	0.01483	+ 0.2	2.004	
	0.0290	47.01	0.02891	- 0.31	1.994	
						2.0
8.5	0.0126	20.475	0.01259	- 0.08	1.998	
	0.0150	24.66	0.01516	+ 0.86	2.022	
	0.0096	15.705	0.00965	+ 0.52	2.012	
						2.010
					Average:	2.004

TABLE V

Valency of Sn-ions Going into Solution from Sn-Amalgam in HNO_3

HNO_3	Input of Sn	Current	Calculated amount of tin assuming Sn^{2+}	Difference	Valency	Average
N	g	amp-sec	g	%		
1.0	0.0224	36.24	0.02229	- 0.5	1.99	
	0.0320	52.35	0.03219	+ 0.61	2.012	
	0.0313	50.44	0.03102	- 0.89	1.982	
	0.0376	60.975	0.03750	- 0.27	1.995	
	0.0449	72.9756	0.04488	- 0.05	1.999	
	0.0395	64.278	0.03953	+ 0.07	2.002	
	0.0423	69.3	0.04262	+ 0.75	2.015	
						1.999
0.5	0.0195	32.22	0.01981	+ 1.58	2.023	
	0.0176	28.44	0.01749	- 0.63	1.987	
	0.0282	45.84	0.02819	- 0.04	1.999	
	0.0152	24.696	0.01519	- 0.08	1.998	
	0.0265	43.71	0.02688	+ 1.43	2.029	
						2.009
					Average:	2.004

TABLE VI

Valency of Sn-ions Going into Solution from Sn-Amalgam in HF

HF	Input of Sn	Current	Calculated amount of tin assuming Sn^{2+}	Difference	Valency	Average
N	g	amp-sec	g	%		
6.0	0.0115	18.912	0.01163	+ 1.13	2.022	
	0.0196	32.25	0.01983	+ 1.17	2.024	
	0.0125	20.28	0.01247	- 0.24	1.995	
	0.0193	31.47	0.01935	+ 0.25	2.005	
	0.0080	12.99	0.00799	- 0.13	1.997	
	0.0226	36.96	0.02273	+ 0.57	2.011	
	0.0140	23.016	0.01415	+ 1.07	2.022	
	0.0190	30.96	0.01904	+ 0.21	2.004	
						2.010
3.0	0.0168	27.03	0.01662	- 1.08	1.979	
	0.0171	27.78	0.01708	- 0.12	1.998	
	0.0075	12.165	0.00748	- 0.27	1.995	
						1.990
					Average:	2.0

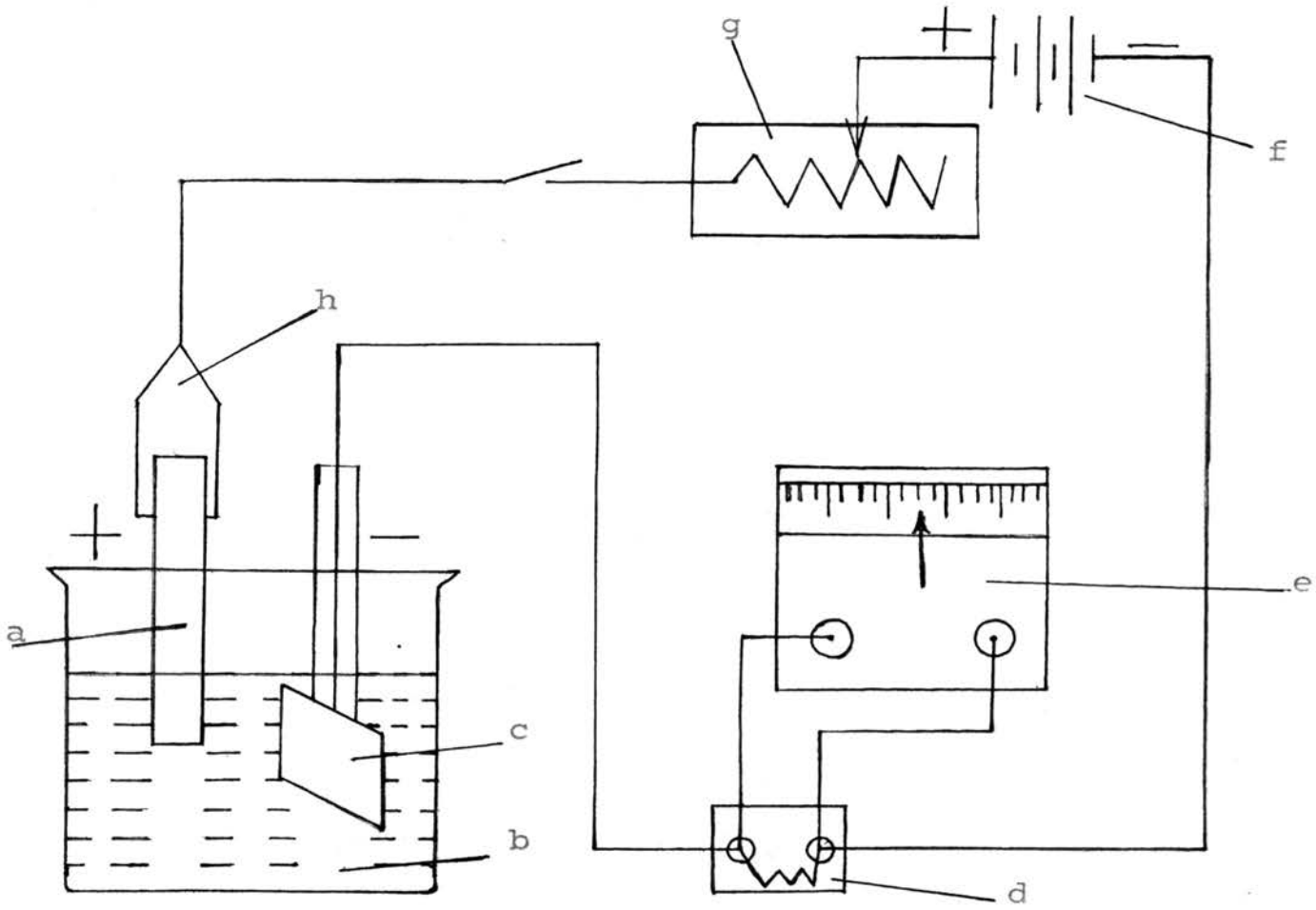
6. Discussion. The valency of Sn ions going into solution from a Sn-amalgam anode in electrolytes of HF, HCl, H_2SO_4, $HClO_4$, H_3PO_4, and HNO_3 was found to be 2.

In all the acids except HNO_3 the current dropped to zero when all tin was dissolved. But in the case of HNO_3, a constant current of about 0.5 milliampere remained steady throughout each test. This steady low current is due to dissolution of mercury in HNO_3, after all Sn is dissolved. Hence, the area in the current versus time plot (Figure 2) was considered only up to the time when the current started to become constant.

A similar experiment with liquid tin-amalgam was tried with 10 per cent NaOH solution. The maximum current noted at the start was about 4.0 milliamperes, which dropped to 2.0 milliamperes in the next minute, and then decreased slowly with time. Even after five hours of dissolution a small amount of current was still flowing. The difficulty involved was of measuring accurately such a small current for so long a time. The valency measurements in NaOH solution, thus, were not possible by this method using no external current.

B. Dissolution Studies with Solid Tin Anode. The experimental setup for anodic dissolution studies is shown in Figure 3. For these experiments a new Honeywell Electronik 18 potentiometer was used which was connected in parallel with a one-ohm shunt to serve as the current recording unit. The anode was made in the form of a stick by melting pure tin in a test tube and pouring it into a small mold made of thin aluminum plate. Before each test, the anode was filed and polished, and then washed thoroughly with water. The surface area exposed to anodic dissolution was measured approximately. A platinized platinum electrode was used as a cathode. A d.c. battery served as a current source which was controlled by a variable resistance box within the circuit.

During anodic dissolution the surface of the tin anode was observed carefully through a magnifying glass. Special attention was given to the observation of film, gas bubble formation, and disintegration. The blackening of the anode surface was noted in HCl, $HClO_4$, and H_2SO_4, but no spalling down of particles. A light yellowish liquid stream of some soluble tin salt was flowing down the anode. Electrolytes in various concentrations were used, and the behavior of the



a. Solid tin anode
b. HCl electrolyte
c. Platinized platinum cathode
d. One-ohm shunt
e. Honeywell potentiometer unit
f. d.c. battery
g. Variable resistance box
h. copper clamp.

Figure 3. Experimental setup for anodic dissolution studies with solid tin anode.

anode was observed at various current densities. Observations are explained in detail in Tables VII, VIII, and IX.

C. Examination of the Black Film Particles. For optical examination a Reichert research microscope was used.

It was observed that pieces of the black film on the anode were less loose at high current densities than at low ones; hence, in order to achieve disintegration a high current density (1200 ma/cm^2) in 1 N HCl was employed so that plenty of the black deposit was formed on the anode. However, particles did not drop down from the anode. Therefore, after electrolytic dissolution the clean anode was taken out and dipped into water, and by gently applying a rubber policeman the black particles were collected. The pieces were then washed several times in distilled water and in acetone, and were finally dried. The residue was transferred to a watch glass and examined under the microscope. At low magnifications, no resolution of single particles could be achieved; hence, an oil immersion objective was applied. In the microscope on the dark background many bright particles with metallic luster appeared in the reflected light which turned opaque in the transmitted. Thus, the presence of metallic particles in the anodic film was

TABLE VII

Anodic Behavior of Pure Tin in HCl

Electrolyte Normality N	Current Density ma/cm^2	Behavior of Anode
0.5, 1.0, 3.0, 6.0, and 9.0	200 and 450	Anode surface turns black. No dropping down of particles. A light yellowish stream of some Sn salt flows down from the anode surface
3.0	5, 10, and 50	the same, but the darkening of anode is very slow
3.0	600 and 900	the same, but the anode surface becomes dark much faster.

TABLE VIII

Anodic Behavior of Pure Tin in H_2SO_4

Electrolyte Normality N	Current Density ma/cm^2	Behavior of the Anode
1.0 and 3.0	450	Anode surface becomes black. No dropping down of particles. No bubbles on the anode surface. A light yellowish stream of some soluble Sn salt flows down from the anode
1.0	1200	black anodic film dissolved and a white film developed. Bubbles developed on the white film of the anode
3.0	900	no black film, but a white film was observed on the anode surface. Current dropped down due to the white film formation and bubbles developed
6.0	450	the same.

TABLE IX

Anodic Behavior of Pure Tin in $HClO_4$ and HNO_3

Electrolyte Normality N	Current Density ma/cm^2	Behavior of the Anode
$HClO_4$ 1.0, 2.5, 5.0, and 10.0	200	Anode surface becomes black. No dropping down of particles. A light yellowish stream of some soluble Sn salt flows down the anode. No bubbles develop on the anode surface
2.0	100, 200 500, and 900	the same
10.0	900	the same
10.0	1500	black film dissolves leaving a very bright anode surface. No further blackening occurs.
HNO_3 1.0	-	Without closing the circuit, a chemical attack on the anode surface was observed and a white tin oxide layer was formed.

partially confirmed. Figures 4 to 7 show the metallic particles under conditions explained beneath each micrograph. Figure 4 shows the agglomerated particles, forming long flakes with bright spots in the reflected light. Figure 5 and 6 reveal tiny randomly distributed bright particles in reflected light. In Figure 7, the same metallic particles appear dark in transmitted light.

Another part of the black anodic deposit was examined by an x-ray diffraction technique. A powder camera was utilized using the asymmetric film loading method, and the x-ray pattern was made with cobalt radiation. This pattern was compared with a pattern made under identical conditions and the same radiation, using pure tin filings. The line-for-line direct comparison confirmed the presence of metallic tin in the film of the anode. The two patterns are reproduced in Figures 8 and 9.

It was difficult to collect the black deposit formed in perchloric acid on the anode. For this reason, the anode surface with the black film on it was examined directly under the microscope. The metal surface, and the black particles extending from it could easily be seen. The distance of the tops from the base could easily be measured with the micrometer screw of the microscope. The corroded surface of tin

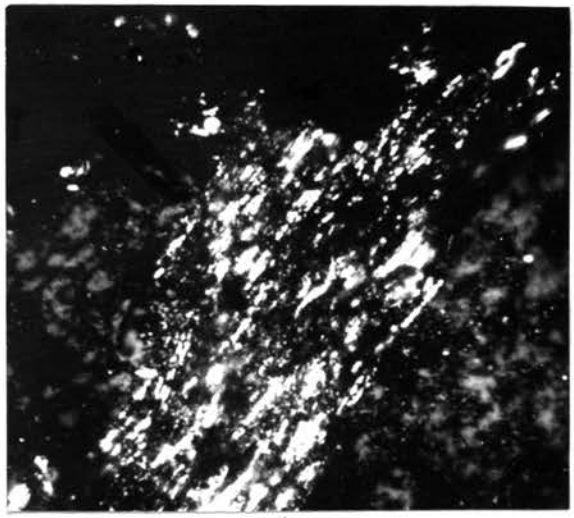


Figure 4. Particles in the black film (bright) obtained from a tin anode dissolving in 1 N HCl at 1200 ma/cm^2. (Reflected light, 1430x, oil immersion objective).

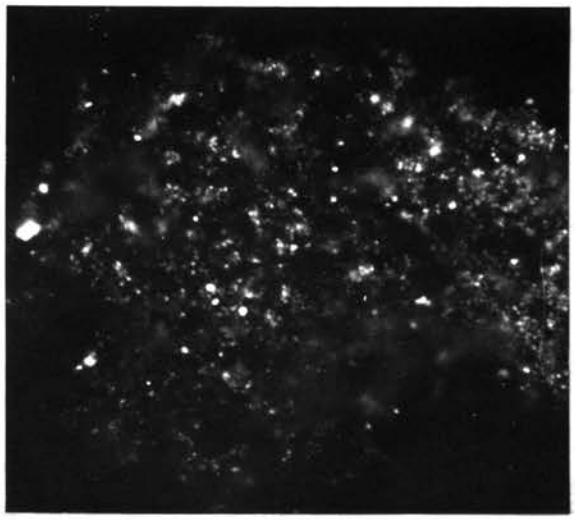


Figure 5. Particles in the black film (bright) obtained from a tin anode dissolving in 1 N HCl at 1200 ma/cm^2. Single bright tiny particles of tin. (Reflected light, 1430x, oil immersion objective).

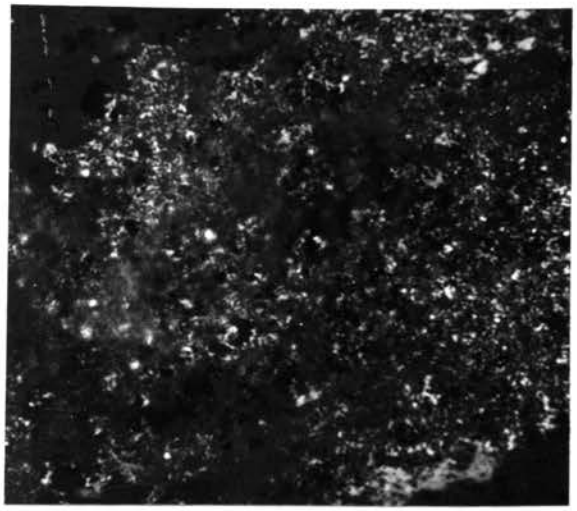


Figure 6. Particles in the black film (bright) obtained from a tin anode dissolving in 1 N HCl at 1200 ma/cm^2. Single bright tiny particles of tin from another collection of particles. (Reflected light, 1430x, oil immersion objective).

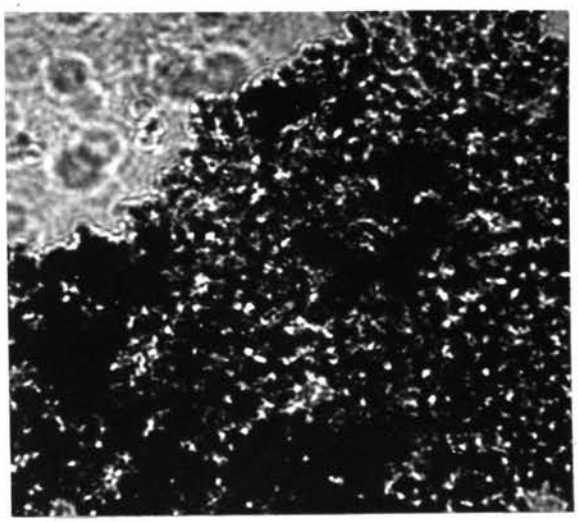


Figure 7. Particles in the black film (dark) obtained from a tin anode dissolving in 1 N HCl at 1200 ma/cm^2. (Transmitted light, 1430x, oil immersion objective).

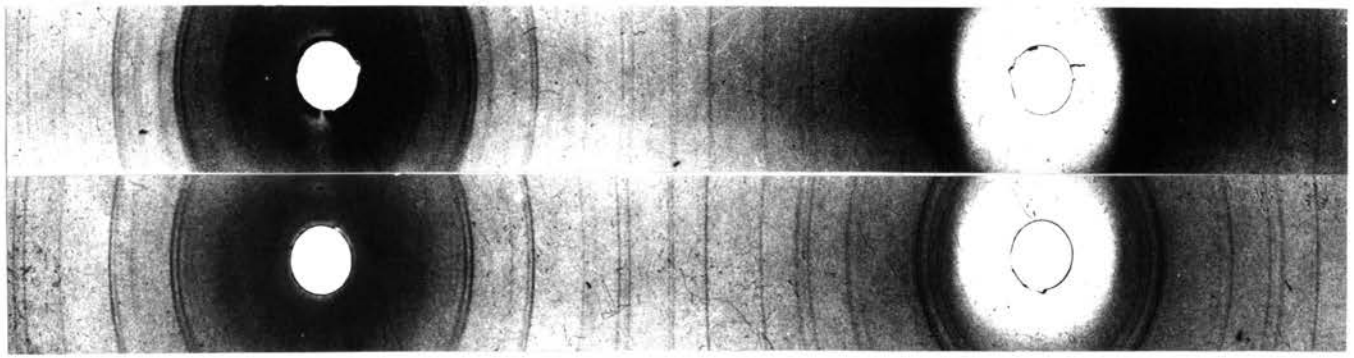


Figure 8 (Above). X-ray diffraction powder pattern of the black deposit collected from a tin anode after dissolving in 1 N HCl at 1200 ma/cm^2. Cobalt radiation for one and one-half hours.

Figure 9 (below). X-ray diffraction powder pattern obtained with pure Sn. Cobalt radiation for one and one-half hours.

anode appeared in alternate bright and dark bands due to unevenness of dissolution; a few microns above this surface the tops of the particles extended from the base and still adhering to it, were visible. The particles are of course metallic and give a black appearance to the anodic film. The shiny tops of the metallic particles were from five microns to sixty microns at various spots above the dissolving anodic surface. Figures 10 to 12 show the micrographs of the metal surface layer and the protruding particles above the surface of the anode under conditions explained beneath each micrograph. Figure 13 shows a schematic view of the tin particles still adhering to the surface of the anode.

D. Quantitative Measurements of the Black Film Formed in HCl. The quantitative measurements of the black film were performed because it was assumed that the black film formed in HCl electrolyte could be a disintegration product of tin detached from the metal surface.

A similar setup as for the qualitative dissolution studies (Figure 3) was also used for the quantitative determinations in 3 N HCl and 1 N HCl. Anodes were made and given a surface preparation in the same way as mentioned before.

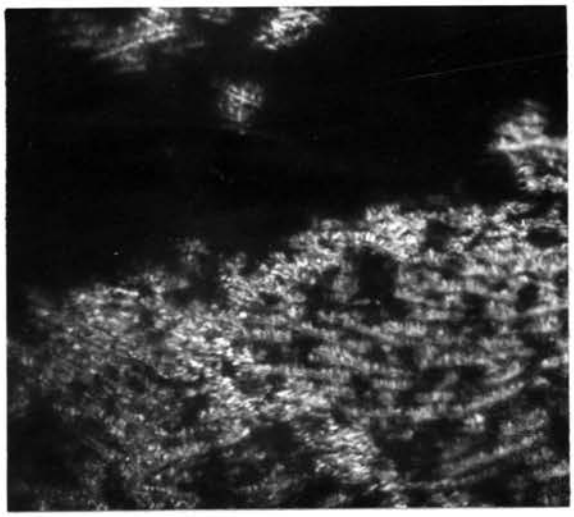


Figure 10. Micrograph of tin anode after dissolution in 10 N $HClO_4$ at 500 ma/cm^2. Alternate bright and dark bands show the structure of metal surface. (750x).

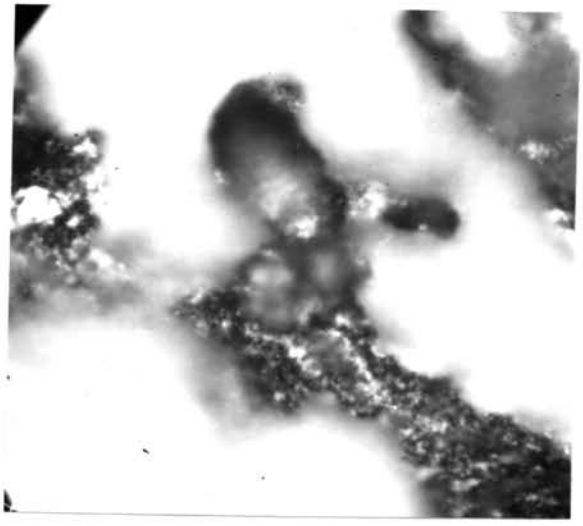


Figure 11. Bright scattered metallic particles on the black film observed directly on the anode. Particles are 16 microns above the base layer of Figure 10. (750x).

Figure 12. Bright scattered metallic particles on the black film observed directly on the anode. Particles are 38 microns above the surface of Figure 10. (750x).

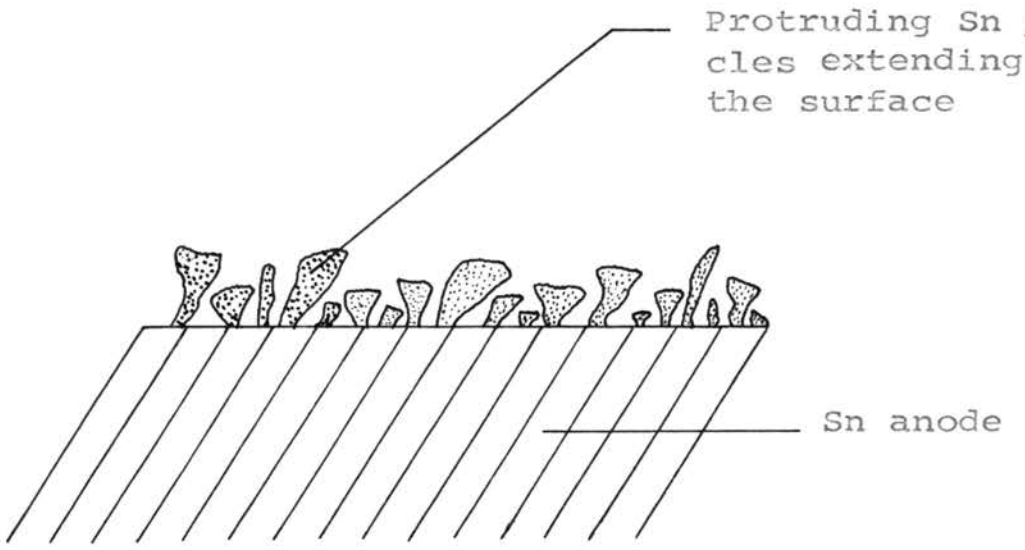


Figure 13. Schematic view of the Sn particles still adhering to the surface of the anode.

All the surface areas exposed to anodic current in the electrolyte were measured (front, back, bottom, and sides). The anode was accurately weighed on an analytical balance before each test. The time and current were automatically recorded on the chart of the Honeywell recording unit. The time was also checked by a stop watch. No particles were dropping down during anodic dissilution from the anode surface, but a fine black deposit was formed on it. After passing the current for a certain time, the anode was taken out and dipped into a beaker of water. The black film was then removed by gently applying a rubber policeman. The anode was washed again with water, and dried with acetone and in hot air. The anode was weighed and the weight loss was calculated by subtracting the final weight from the original. This weight loss (W) of the anode is then due to (i) coulombs passed, (ii) removal of film, (iii) self dissolution (without current).

The weight loss due to coulombs passed and self dissolution were calculated separately as explained below:

1. Calculation of the expected weight loss from coulometric data. The total amount of coulombs passed was calculated from the area under the curve recorded by the Honeywell unit, and the weight loss in grams (W_q) from these

data according to Faraday's law for each test from the equation:

$$W_q = \frac{q.A}{F.n}$$

where q is the total amp-sec passed,

A - the atomic weight of tin (=118.69),

F - Faraday's constant (=96,487 amp-sec),

n - normal cationic charge of Sn (=+2).

2. Calculation of self-dissolution (w_s). A similar piece of tin stick after the proper surface preparation was dipped into 3 N HCl for 3 hours (without passing any external current) with 2 cm^2 area exposed to the electrolyte. The average weight loss of four tests due to the self-dissolution was found to be 0.0128 g/2 cm^2.3 hrs, that is, 0.0021 g/cm^2.hr, assuming that the rate was even during the three hours. The amount of self-dissolution (w_s) was calculated for each of the anodic dissolution tests by multiplying the mentioned rate factor with time and area involved.

3. Calculation of weight per cent of black particles formed. The percentage of black particles formed on the anode was then calculated as follows:

$$\text{Black particles formed in } \% = \frac{W - (W_q + w_s)}{W} \times 100$$

where W is the total weight loss of the anode in g,

W_q - weight loss from coulometric data in g,

w_s - weight loss due to self-dissolution in g.

The quantitative study was performed with a current density as low as 5 ma/cm^2, because Rumpel, Davidson, and Kleinberg obtained lower valencies at current densities lower than 10 ma/cm^2. The study however, was extended up to 900 ma/cm^2. Beyond 900 ma/cm^2, it was difficult to keep the current density constant due to the rapid decrease of the surface area of the anode stick. The results are summarized in Tables X and XI. Different self-dissolution data (w_s) in these tables are due to the fact that area and time of dissolution was different for each test.

TABLE X

Quantitative Results of the Black Film

Studies in 3 N HCl

Current density	Total wt. loss of anode after dissolution	Expected wt. loss from coulometric data	Wt. loss due to self-dissolution	Black Particles formed
ma/cm^2	W	W_q	W_s	%
5	0.0847	0.0765	0.0092	- 1.18
	0.0858	0.0770	0.0092	- 0.46
	0.0842	0.0766	0.0092	- 1.9
	0.0893	0.0770	0.0092	+ 3.47
	0.0836	0.0783	0.0080	- 3.23
			Average:	- 0.66
10	0.0182	0.0167	0.0015	0
	0.0173	0.0160	0.0014	- 0.57
	0.0178	0.0161	0.0014	+ 1.68
	0.0171	0.0154	0.0014	+ 1.75
	0.0169	0.0155	0.0014	0
			Average:	+ 0.57
20	0.0324	0.0307	0.0014	+ 0.92
	0.0338	0.0321	0.0014	+ 0.88
	0.0353	0.0334	0.0015	+ 1.13
	0.0327	0.0311	0.0014	+ 0.61
	0.0307	0.0290	0.0013	+ 1.3
			Average:	+ 0.96
50	0.0735	0.0715	0.0013	+ 0.95
	0.0700	0.0683	0.0012	+ 0.71
	0.0791	0.0764	0.0014	+ 1.64
	0.0731	0.0709	0.0013	+ 1.23
	0.0658	0.0642	0.0012	+ 0.6
			Average:	+ 1.03

TABLE X
(Continued)

Quantitative Results of the Black Film

Studies in 3 N HCl

Current density	Total wt. loss of anode after dissolution	Expected wt. loss from coulometric data	Wt. loss due to self-dissolution	Black particles formed
ma/cm^2	W	W_q	W_s	%
100	0.1142	0.1129	0.0010	+ 0.26
	0.1104	0.1085	0.0010	+ 0.81
	0.1013	0.0997	0.0010	+ 0.59
	0.1573	0.1555	0.0014	+ 0.25
	0.1490	0.1472	0.0013	+ 0.33
			Average:	+ 0.44
300	0.3854	0.3809	0.0012	+ 0.85
	0.4276	0.4247	0.0013	+ 0.37
	0.0634	0.0622	0.0002	+ 1.57
	0.0671	0.0663	0.0002	+ 0.89
	0.0612	0.0599	0.0002	+ 1.8
			Average:	+ 1.09
600	1.0154	1.0021	0.0015	+ 1.16
	0.7682	0.7550	0.0017	+ 1.5
	0.6810	0.6675	0.0010	+ 1.83
	0.8349	0.8236	0.0015	+ 1.17
			Average:	+ 1.41
900	0.6150	0.6074	0.0008	+ 1.1
	0.5972	0.5920	0.0006	+ 0.77
	1.3307	1.3178	0.0016	+ 0.85
	1.5538	1.5271	0.0015	+ 1.62
			Average:	+ 1.08

TABLE XI

Quantiative Results of the Black Film

Studies in 1 N HCl

Current density	Total wt. loss of anode after dissolution	Expected wt. loss from coulometric data	Wt. loss due to self-dissolution	Black particles formed
ma/cm^2	W	W_q	W_s	%
100	0.0384	0.0380	0.0002	+ 0.52
	0.0382	0.0380	0.0002	0
	0.0380	0.0376	0.0002	+ 0.52
			Average:	+ 0.35
500	0.1869	0.1869	0.0002	- 0.1
	0.0888	0.0882	0.0002	+ 0.45
	0.0897	0.0896	0.0002	- 0.11
			Average:	+ 0.08
700	0.3215	0.3223	0.0002	- 0.31
	0.1307	0.1297	0.0002	+ 0.61
	0.1319	0.1315	0.0002	+ 0.15
			Average:	+ 0.15
900	0.3254	0.3254	0.0002	- 0.06
	0.1701	0.1694	0.0002	+ 0.29
	0.1662	0.1662	0.0002	- 0.12
			Average:	+ 0.03

IV. DISCUSSION

The purpose of this investigation was to determine whether or not tin ions enter solution with a valency less than two, and to obtain experimental data concerning behavior of a tin anode in various acid solutions.

The anodic dissolution of tin was studied in the acids HCl, H_2SO_4, $HClO_4$, H_3PO_4, HNO_3, and HF of various concentrations. Valencies were determined by dissolving tin from liquid tin-amalgams, where the possibility of disintegration was eliminated. No external current was used. The normal valency of 2 was established in all of the above mentioned acids.

For the anodic oxidation of tin, Rumpel, Davidson, and Kleinberg had postulated univalent tin ion formation as the first step, all of which are oxidized at the anode in the case of non-oxidizing electrolytes.

The observed valency of 2 in the present investigation with non-oxidizing acids HCl, H_2SO_4, $HClO_4$, H_3PO_4, and HF agrees with their result in non-oxidizing electrolytes such as NaCl, $NaC_2H_3O_2$, and $SnCl_2$.

However, the formation of monovalent tin ion as the first step of anodic dissolution could not be supported

because it appears improbable that all Sn^+ ions could return to the anode against the solution pressure of tin; instead, a part could reduce hydrogen ions to gas ($Sn^+ + H^+ \longrightarrow Sn^{2+} + 1/2\ H_2$), in which case a lower valency could have been observed.

Moreover, they explained the observed lower valencies (1.02 to 1.40) in $NaNO_3$ electrolyte in the light of the above theory, by suggesting that some intermediate univalent tin ions are oxidized chemically to the bivalent state by the nitrate ions whereas, some are oxidized electrolytically.

But in the present investigation, a valency of 2 was obtained in HNO_3 electrolyte directly, though HNO_3 is an oxidizing acid. If there would have been intermediate Sn^+ ion formation some of them should have been oxidized chemically to the bivalent state by NO_3^- ions of HNO_3 and a deviation from Faraday's law should have been observed. This, however, was not the case.

Thus, the postulation of undetectable intermediate monovalent tin ion formation could not be supported by the present investigation.

Experiments were conducted with a solid tin anode to study the possible disintegration phenomena in HCl, H_2SO_4, $HClO_4$, and HNO_3 at various current densities. In the case of HNO_3, chemical attack occurred without any external current, forming a white tin oxide layer on the anode surface, hence, no further disintegration studies were made with HNO_3 electrolytes.

Darkening of the anode surface was observed during electrolytic dissolution in HCl, H_2SO_4, and $HClO_4$, but there was no spalling down of particles.

After electrolytic dissolution in 1 N HCl at 1200 ma/cm^2 the black film of the anode was removed by the gentle use of a rubber policeman. After thoroughly washing the residue with water and drying, it was examined under the microscope. Bright scattered agglomerated particles were observed at high magnification in reflected light. The particles turned opaque in transmitted light; thus, some metallic particles were present in the pieces of film. An x-ray pattern obtained with another part of the film proved conclusively the presence of tin.

The black anode surface formed in $HClO_4$ electrolyte was examined directly under the microscope. Long bright and dark bands indicated the uneven, corroded metal surface

formed during dissolution. A few microns above the surface some bright particles were observed which still were in contact with the anode surface. If removed with the policeman metallic Sn could be proved to be present. These metallic particles extended five to sixty microns above the metallic surface.

Quantitative studies were performed in 3 N and 1 N HCl. The results obtained as explained in Tables X and XI, are within 1.41 per cent, which is the weight percentage of black particles removed from the anode surface by the rubber policeman. A negative result of - 0.73 per cent was obtained at 5 ma/cm^2 which could be due to experimental error. From these results it appears that the metallic tin particles in the film are still loosely in contact with the anode surface even at the end of electrolysis,and thus, finally dissolve electrolytically without leaving the anode.

It is evident that the black metallic deposit originated from the tin anode. It is most possible that the anodic dissolution proceeded through uneven attack of the Sn surface leaving mountains of Sn on its surface. There are always preferential attacks at the grain boundaries, deformation twins, and other imperfections which cause some portions of

the tin to dissolve more readily than the other ones. The remaining mountains constitute the black film on the anode surface. If undermining of some portions of the film occurs, fallout of particles or "disintegration" may be observed. Normally such a disintegration of Sn anodic surfaces does not occur.

V. SUMMARY AND CONCLUSIONS

Tin dissolves anodically in aqueous acid solutions producing Sn^{2+} ions only. There was no deviation from Faraday's law within the error limits of the measurements.

The fallout of particles or "disintegration" of Sn does not occur during anodic dissolution in HCl, $HClO_4$, and H_2SO_4. However, during dissolution in these electrolytes a black metallic deposit is observed in the form of tin protruding from the anode surface. The formation of this black deposit was possibly the first step which would lead to disintegration if undermining of some portions of the film occurred.

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VII. VITA

Mrityunjoy Dutta was born at Durgapur, West Bengal, India on February 15, 1937. He received his elementary and high school education at Durgapur, India. He entered Calcutta University in 1953 and received a Bachelor of Science degree in Physics, Chemistry, and Mathematics in 1957.

In January 1962, he entered the University of Missouri at Rolla. He was granted a Bachelor of Science degree in Metallurgical Engineering from this institution in January 1964.

In February 1964, he entered the graduate school of the University of Missouri at Rolla to pursue the degree of Master of Science in Metallurgical Engineering and was appointed as a Research Assistant.